

THE INTERACTIONS OF GASES WITH COAL: STRUCTURAL INFERENCES*

E. L. Fuller, Jr.

Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Current and proposed efficient uses of coal involve the interaction of fluid phases with coal or coal chars. This study deals with the mode of interaction of gases with coal from the standpoint of analyses related to the structure of coal and implications pertinent to mechanisms of fluid phase reactions. "Coal is an amorphous substance and it is difficult to define its structure.... The fundamental chemistry of coal liquefaction will probably remain poorly understood until coal structure is better defined." (1) There is considerable effort to define this structure in terms of internal surface area and microporosity in studies of vapor (2) (3) (4) and liquid (5) interactions. Microgravimetric sorption equipment and techniques (6) have been used to elaborate the thermodynamics and kinetics described in this text. The coal, high-volatile A-bituminous Illinois No. 6, was obtained at the mine face and stored in argon prior to grinding (< 200 mesh) in argon.

Sorption-desorption isotherms are given in Figures 1-3 for (a) N₂ [classical vapor for surface area determinations], (7) (b) CO₂ [often suggested as a means of determining the "effective area" of coal], (2) and (c) H₂O [of interest because of its inherent content in coal and its potential use as a reactant at elevated temperatures]. Classical BET (7) analyses of the data indicate a marked disparity in the apparent specific surface area of this coal: 2.8, 128, and 68.2 m²/gm for N₂, CO₂, and H₂O respectively. (The N₂ value is consistent with the predominant 1-10 μm size distribution observed microscopically.) These values vary markedly and seem to be "dominated by dipolar and London forces" as noted in related studies. (5)

Alternate analyses of the isotherms can be performed in terms of the sorption potential: $\epsilon = -RT \ln P/P_0$ (Polyani, circa 1914). (8) Various relationships between this quantity and the sorbate concentration, Γ , have been used. (8)

In terms of the chemical (9) and physical structure (10) of coal [polynuclear aromatic rings with methylenic linkages with numerous polar functional groups, oriented to some extent in parallel layers] one can readily envision the energetics of the sorption process to follow a distribution of the type (11) (12) $\epsilon = \epsilon^0 e^{-a\Gamma}$. If we were to view the substrate as a yielding "soft" electronic structure (extensive pi bond network with the polar entities rather randomly distributed), we would anticipate considerable energetic (electronic) perturbation by the sorption processes. Then a distribution like that above would be expected to apply. Such a model is akin to the image forces induced in the mobile electrons when sorption occurs on metals. (13) Our experimental results follow the trends inherent in this model for each of the gases. The data for water is shown in Figure 4. Many have attributed the variation of sorption capacity to temperature effects on the diffusion rate by virtue of very large activation energy for diffusion into the coal matrix. (14) Our kinetic results were not amenable to interpretation in terms of diffusion mechanisms. However good adherence to a mass action second order (15) was noted. An example is given in Figure 5 for one incremental pressure change employed in the construction of the water isotherm. One should note that this data was obtained under isobaric, controlled pressure, conditions ($\pm 0.0001 P_0$) for the time required to evaluate the steady state condition at each chosen pressure. The technique and evaluation

*Research sponsored by the Office of Basic Energy Sciences, Division of Material Sciences, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

procedures are outlined elsewhere.(16) Carbon dioxide results were more complex and indicated that there were two second order processes in play.

With such assurance that we are dealing with steady state conditions, based on this kinetic continuity and accountability, we can confidently attribute the desorption retention to structural changes induced in the coal matrix. This retention is totally removed in vacuo [10^{-10} P₀] albeit quite slowly [24+ hours]. Such behavior could arise if trace amounts of a second vapor, i.e., H₂O in N₂, were adsorbed. We have employed 99.9995% N₂ and have not noted the retention phenomena on rigid substrates in this microgravimetric system. Many related systems show a similar retention where there is a "change in 'structural' arrangement in the molecular network".(17)

We can gain further insight into the process in terms of the molecular properties of the sorbate molecules. If there are induced effects in the substrate, one would anticipate the magnitude of the energy of interaction to be proportional to energy arising from the intermolecular forces between two sorbate molecules in the gas phase.(18) There is good correlation between the dispersion ($\frac{3}{4} \alpha^2_{\text{hy}}$) and electrostatic ($\frac{2}{3} \frac{\mu^2}{kT}$) energies and the ϵ° term inherently evaluated in our treatment of the sorption isotherms in the form of Figure 4. The correlation is shown in Figure 6.

These results are to be contrasted with that predicted for sorption onto a rigid ("hard") electrostatic field (13) and noted experimentally as a first power relation (19) in polarizability (α) and second power in dipole moment (μ).

In light of these studies and the marked swelling properties of coal, even on CO₂ and CH₄ sorption,(20) we must question the existence of a fixed definable pore structure and/or internal surface area of coal. Further analyses on this and coals of varied rank are warranted. One would anticipate that the results might range from the marked sorption swelling of cellulosic materials to the intercalation phenomena noted for graphite.(17)

Acknowledgment: This work is the result of the diligent and conscientious efforts of the members of the Massachusetts Institute of Technology School of Chemical Engineering Practice, M. M. Alger, O. K. Chow, M. Z. Khan, and S. M. Senkan.

References

1. W. H. Wiser and L. L. Anderson, Ann. Rev. Phys. Chem. 26 339 (1975).
2. J. Medik, Fuel 56 131 (1977).
3. K. Tomkow et al., Fuel 56 101 (1977).
4. Z. Spitzer et al., Fuel 56 313 (1977).
5. J. W. Larson et al., Fuel 57 309 (1978).
6. E. L. Fuller, Jr. et al., Prog. Vac. Sci. Tech. 3 71 (1974) and 1 265 (1972).
7. S. Brunaur, P. H. Emmett and E. Teller, J. Am. Chem. Soc. 60 309 (1938).
8. A. W. Adamson, "Physical Chemistry of Surfaces," Wiley, p. 575 (1976).
9. (a) G. R. Hall and L. B. Lyon, Ind. Eng. Chem. 56 36 (1962); (b) W. H. Wiser, Ref. 1 (1975).
10. P. B. Hirsch, Proc. Roy. Soc. 226A 143 (1955).

11. J. H. deBoer and C. Zwikker, Z. Phys. Chem. B3 407 (1929).
12. R. S. Bradley, J. Chem. Soc. (1936) 1799.
13. W. A. Steele, "The Interactions of Gases with Solid Surfaces," Ch. 2, Pergamon (1974).
14. S. P. Nandi and P. L. Walker, Fuel 43 385 (1964).
15. S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill (1960).
16. E. L. Fuller, Jr., "Microgravimetric Studies of Catalysts in Microweighing in Vacuum and Controlled Environments," editor, A. W. Czanderna, Elsevier (in press, 1978).
17. P. J. Sereda and R. F. Fedlman, Ch. 24 in "The Solid-Gas Interface," editor, E. A. Flood, Vol. II, Marcel Dekker (1967).
18. J. O. Hirschfelder et al., "Molecular Theory of Gases and Liquids," Ch. 13, Wiley (1954).
19. E. L. Fuller, Jr. and P. A. Agron, "Reactions of Atmospheric Vapors with Lunar Soils," ORNL-5129, March 1976.
20. (a) H. Briggs and R. P. Sinha, Proc. Royal Soc. Edin. 53 48 (1933); (b) A. Czaplinski, Arch. Gorn. 16 227 (1971); (c) E. A. Flood and R. H. Heyding, Can. J. Chem. 32 660 (1954).

By acceptance of this article, the publisher or
recipient acknowledges the U.S. Government's
right to retain a non-exclusive, royalty-free
license in and to any copyright covering this
article.





